

22nd.August 2012

Three small systems showing probable room-temperature superconductivity

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ABSTRACT

I shall discuss three small systems in which I think room-temperature superconductivity has been observed, in the hope that experimentalists will be persuaded to try to reproduce and extend results on some or all of the three systems mentioned. These are: 1. Narrow channels through films of oxidised atactic polypropylene (OAPP) and other polymers. 2. Some multiwalled carbon nanotubes or mats of nanotubes. 3. Sandwich structures based on CdF_2 . The main emphasis will be on polymer films.

Keywords: Room-temperature superconductivity, bipolarons, polymer films, carbon nanotubes, CdF_2 sandwich structures.

PACS: 73.61.Ph, 74.20.Mn, 74.78.Bz, 71.38.Mx

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1. Introduction

Small systems or systems with small subsystems are advantageous for superconductivity in two ways: First because it is easier to get Bose-Einstein condensation if there is separation in energy between the lowest state of the system and excited states; secondly because it is easier to get pairing at low carrier concentrations in low dimensions, since, in the BCS regime there is an enhanced density of states at low carrier concentrations in one and two dimensions compared with three, and, in the BEC regime because bipolarons can form more easily in low dimensions. The separation in energy between the ground state and excited states mentioned in the first point above is normally only a significant effect if the density of electronic states as a function of energy is such that condensation cannot occur in an infinite system, but in such cases it can have a large effect. For instance, for Bose condensation in small arrays of filaments if a simple quadratic dispersion is assumed for the bosons, then the condensation temperature at small lengths L can increase approximately as $(1/L)$, as may be seen from Eqs. (21) and (2) of [1]. On the negative side it is not possible to get infinite conductivity in quasi one-dimensional systems because of phase slips, and only a small fraction of a Meissner effect is possible if the transverse dimensions are of the order of or smaller than the magnetic-field penetration depth. Also on the negative side, superconductivity in small systems will only have small-scale applications such as switching devices or interconnections in electronics, unless small systems

can be combined weakly into larger ones without losing the advantages of the original small sizes.

Two of the small systems I shall mention involve arrays of quasi one-dimensional systems, although in one of the cases the existence of these arrays is based on theory rather than experiment, and the third is a quasi two-dimensional sandwich system. The dates of the first claims of room-temperature superconductivity in the three systems are separated by about ten years, the first in 1988 and published in the open literature in 1989, the second in 1999, and the third in 2009.

2. Two thin-film systems and one nanotube-based system

In 2009, 2010 and 2012, Bagraev and coworkers gave evidence for superconductivity above room temperature in a CdF_2 -based sandwich system, involving two 3 nm thick boron doped layers sandwiching a 2 nm thick p -type layer of CdF_2 , all on top of a 1 mm thick n -type substrate [2, 3, 4, 5]. Their work includes evidence for zero resistance at 319 K, large diamagnetism starting at somewhat higher temperatures, tunnelling evidence of an energy gap of about 102 meV, and peaks in the specific heat at temperatures close to those of the resistance drop.

After first suggestions of possible room-temperature superconductivity in multi-walled carbon nanotubes by Tsebro and coworkers [6], Zhao and coworkers gave evidence from 2001 [7, 8, 9] from their own results and published data of others that superconductivity occurs for temperatures up to over 700 K in multiwalled nanotubes or mats of single-walled or multiwalled nanotubes. The evidence is from resistance analysed by a slightly modified version of the Langer-Ambegoakar-McCumber-Halperin (LAMH) theory of resistance due to phase slips, from diamagnetic susceptibility much reduced from a full Meissner effect due to magnetic field penetration depths being larger in magnitude than tube diameters, tunnelling results showing large energy gaps, and analysis of the temperature dependence of Raman data for phonons of energy close to the energy gap. In a review paper [8], Zhao gives reasons for the extraordinarily wide variation of T_c in different nanotubes or nanotube mats. The main contributions to the variation are: 1. Different Luttinger-liquid parameters due to different amounts of screening because of different surroundings of any nanotube; and 2. Variations in carrier concentrations.

There are five reasons for thinking that narrow channels through films of oxidised atactic polypropylene (OAPP) are superconducting at room temperature:

1. Measurements with In microcontacts on top of films on a Cu substrate show that at some points resistance is fairly low, and, within the spread of values, is approximately independent of the film thickness [10, 11]. There is also evidence [11] that superconductivity persists up to at least 429 K in currents of 0.5 A.
2. Estimates of the conductivity by direct [12] and indirect [13] methods are several orders of magnitude larger than that of Cu. I have some difficulty in understanding how the authors of [12] obtained their direct results on conduction by four-probe measurements, but I am more confident in the indirect estimates of conductivity discussed in 4. below.
3. The high conductivity is destroyed by non-thermal means by pulsed currents of the order of 60 A through channels or groups of channels, implying that the critical current density lies between 10^8 A cm^{-2} and about $5 \times 10^9 \text{ A cm}^{-2}$, depending on whether the whole contact area or the estimated diameter of a single channel is used to convert a critical

current to a critical current density. Probably the density is somewhere between these values, because the method of measuring with pulses of gradually increasing magnitude may cause several channels to merge before the critical current is reached.

4. The thermal conductivity measured with contacts to the channels is not significantly different from that with contacts to insulating regions of the films [14], implying that the electronic contribution to the thermal conductivity is very small, and that the the Wiedemann-Franz law is violated by several orders of magnitude, as expected for a superconductor.

In the pulsed current measurements mentioned above, with use of the thermal conductivity results, it is estimated that, for pulse lengths of the order of a microsecond, the heat front could only propagate $0.3 \mu\text{m}$ into the channel, a much smaller distance than the channel length of about $30 \mu\text{m}$. The heating of the channel must be less than about 1000 K since otherwise the polymer would decompose in 1-10 seconds at a pulse repetition rate of 25 Hz used in some of the pulsed measurements, and this leads to an indirect estimate of the conductivity in terms of the pulse length, diameter of the channel, and the critical current, which turns out to be several orders of magnitude greater than that of Cu.

5. There is large diamagnetism in some samples of OAPP at low fields as shown by magnetisation measurements [11, 15] and by occasional spontaneous jumps of films to lower-field regions in inhomogeneous fields [16]. Both effects are thought to be related to superconducting channels which join at their ends to form closed loops. Only a small diamagnetism can be expected due to the Meissner effect for the systems being studied, both because there is never more than about 1% of the film occupied by conducting channels and because there is expected to be a further reduction by a factor of the order of 100 if the magnetic-field penetration depth is of the order of the channel radii. However, I have been able [17] to interpret details of the magnetisation versus field curves obtained by Rogachev and Grigorov in 2000 [15] for fields below a metamagnetic transition in terms of a theory of Shoenberg [18] for induced currents in closed loops of type I superconductors below the critical field. This was assumed in [17] to apply to type II superconductors with no pinning at fields below H_{c1} , but I now think that it will also apply even with pinning for fields below the field H_R at which resistance arises. The fits with a model with two types of loops to adjusted data after corrections for an estimated superparamagnetic contribution from channels which do not form closed loops deduced from results for magnetism on the next day after large fields had been applied are shown in Fig. 1 of [17]. Two results of interest which come out of the fitting and analysis are that $H_R \approx 5260 \text{ Oe}$, and that the diameter of the cross section of the channels is less than about $1.52 \mu\text{m}$, compared with a value of about $1 \mu\text{m}$ estimated by Grigorov and coworkers in 1990 [13]. The initial susceptibility in the first film corresponds to about 0.7 % of a full Meissner effect, and I know of no mechanism not involving superconductivity which can give such a large diamagnetism. Estimates of H_{c1} based on theory of Alexandrov [19, 20] for bosonic superconductors combined with parameters obtained in the latest version [21]¹ of my model for superconductivity in OAPP are much smaller than the value of H_R given above,

¹The bracketing in Eq. (1) of this paper was incorrect. Also the directions of the aligned dipoles were stated incorrectly in lines 3 and 9 of section 4, and, in subsection 14.14, last line, "greater than $1.52 \mu\text{m}$ " should be replaced by "less than $1.52 \mu\text{m}$ ". An erratum has been submitted about Eq. (1). The correct version of this equation may also be seen in v2 of the preprint arXiv: 1106.0716

and I now interpret the value as that of the depinning field.

For the diamagnetism and for metamagnetic transitions which occur both in OAPP and in polydimethylsiloxane (PDMS) there are often time-dependent effects over periods of days, and application of a field above a critical value may disrupt this time dependence (see e.g. [22]).

The theory of Grigorov and coworkers [23, 24, 25] for why conducting channels exist in polar elastomers such as OAPP involves an unusual type of polaron where rotatable dipolar groups become aligned within a certain radius towards or away from an excess charge. Also, for a high ratio of static and high-frequency dielectric constants, these polarons can coalesce to form linear strings called superpolarons, and the superpolarons coalesce to form conducting channels.

The latest version of my model for the superconductivity [21]¹ is modified considerably from an early version [26]. Both versions involve Bose condensation in an array of nanofilaments. Two differences from the earlier version are: 1. An assumed Bogoliubov form for the dispersion of the bosons, with an effective bosonic potential μ_B at T_c which is considerably smaller than that at $T = 0$; 2. Larger numbers of nanofilaments in the smallest superconducting channels, based on an estimate of the resistance for an N-S-N system with good contacts, where the superconducting system consists of an array of nanofilaments (cf. [27]), and comparison with resistance histograms mentioned before. Although there can be pairing in a single nanoflament, the usual objections to long-range order in one dimension prevent the occurrence of superconductivity. Also, since the fractional reduction of T_c due to resistance from phase slips in arrays depends on (the array cross section)^{-2/3} [28] at least for BCS superconductivity, small arrays cannot produce high- T_c 's.

My model makes a lot of use of a 1991 paper by Grigorov [25] for ferromagnetic superpolarons, and assumes that pairs form in the superpolaron strings by attraction via either plasmons or high-frequency phonons. Most of the parameters are determined by minimising a weighted sum of moduli of differences between calculated values and best-fit-values of parameters occurring in equations determining theoretical or experimental constraints, with weightings determined by how accurate I think the constraints are. For the parameters I find, the limiting T_B for large n_T is not much higher than room temperature, and so, as in an earlier paper [26], to explain the apparently considerably higher T_c 's which occur when significant currents are applied, we have to invoke decreases in transverse masses due to current-current interactions decreasing the transverse lattice constant in the soft materials being discussed. Alternatively it is possible that a method I used to estimate μ_B gives too high a value. For a much smaller μ_B we would find a relatively high value of T_B for large-diameter channels.

There are some similarities and some differences from treatment of arrays of nanowires by Bianconi and coworkers [29, 30]. Differences in their treatment include: 1. Coupling weak enough for the carrier concentrations studied for a BCS-like theory to apply, as opposed to the BEC regime considered by me. 2. Parameters such that the second or third quantised level with respect to transverse motion in a nanowire becomes occupied, whereas in my model for OAPP only the ground state is occupied. (For the model of Grigorov for nanofilaments in OAPP, the Fermi energy before pairing is approximately proportional

to the square of the reciprocal of the nanofilament radius, and it is not possible to find a situation in which the second quantised level becomes occupied, except possibly for very thin films in which charge injection may increase the carrier concentration).

We make conjectures about the reasons for stronger pairing and higher T_c 's in OAPP than in established high-temperature superconductors. A first difference is the smaller high-frequency dielectric constant (2.2 in polypropylene) which permits stronger coupling to plasmons (see e.g. [31]), and also, if combined with a high static dielectric constant, stronger coupling to polar optical phonons. A second difference is that there is not expected to be any significant increase in masses due to correlation, permitting a higher condensation temperature in the BEC regime for a given carrier concentration and strength of coupling with bosons. A third difference is that there are very high energy phonons in polypropylene (up to 0.39 eV), which is helpful if pairing is mediated by phonons. Eight suggestions of properties useful for very high-temperature superconductivity were made on pp 1945-6 of [26].

The parameters of the model I used for OAPP indicate that this system is on the BEC side of the BCS-BEC crossover, but not very far from it. Maximum T_c 's near the crossover are common to many models. The crossover in superconductors was first studied in 1969 [32]² after work of Labbé et al. in 1967 [33] had drawn attention to the fact that, for strong pairing and low carrier concentrations, shifts in the Fermi level due to pairing have to be considered. In 1980 Leggett [34] discussed the crossover in an atomic system. Studies of the crossover have proliferated since 2004 when it was observed by several groups in atomic gases (see e.g. references in [35]).

The first claim of a BEC superconductor was made by Ogg in 1946 [36].³ Early indications of a superconductor on the BEC side of the transition were obtained in 1986 [37, 38, 39] in one ceramic sample of SrTiO_3 with 3% of Ti replaced by Zr. Some authors (see e.g. [40, 41]) think that at least the underdoped cuprates are BEC superconductors. Most recent evidence of a crossover has been found for one of the bands in multiband superconductors due to the Fermi level being close to the bottom of a second band in a quantum well [42], or for small occupation of one of the bands for some other reason [43].

It may be of interest to speculate as to why the experimental results on the systems mentioned have not been reproduced by other groups. We suggest that this is due to a combination of some or all of the following factors: (a) Not many people being aware of the results; (b) Those that are aware not believing the interpretations given; (c) The commonly held belief that, if results are not confirmed quickly, then they are not likely to be valid; and (d) Some prejudice against the possibility of room-temperature superconductivity. In the case of Bagraev and coworkers it is probable that factor (a) is dominant. Three of the four papers of theirs that I mentioned appeared in a journal that is probably not read widely in the superconductor community, and none of the four papers mention superconductivity in their titles. In the case of Zhao and coworkers, since they include experimental results of others in their analyses, factors (b) and (d) seem more

²I should like to give a belated acknowledgement to G.L. Sewell for a useful conversation in the mid 1960's, in which he drew my attention to the fact that pairing does not necessarily give rise to superconductivity.

³A few years ago a large group from University College, London, was trying to reproduce Ogg's results, but does not appear to have published any results.

likely. A difficulty, felt by me at one stage, is the claimed extraordinarily wide variation of T_c between different nanotube-based systems, but Zhao addresses this problem in his review article [8]. Zhao has a good reputation for work on the cuprates, but, despite he and coauthors writing preprints since 2001 on room-temperature superconductivity in nanotube-based systems, only one journal paper by them has appeared on the subject up till now. In the case of Grigorov and coworkers, I think it is probable that there is a more even distribution between the four factors.

3. Conclusions

To summarise, room-temperature superconductivity appears to have been observed in several small systems. I think it is important that experimentalists should try to reproduce and extend the results. For each of OAPP and the CdF_2 -based sandwich system, most of the results have been obtained by only one group, although A.N. Ionov and coworkers have done a lot of work since 1999 confirming that superconductivity occurs in superconductor-polymer film-superconductor systems at temperatures below the superconducting T_c of the electrodes, and find that this is not due to the proximity effect. (See e.g. [44] and references therein and in my 2011 paper). A recent paper on PDMS not referred to in [21] is [45], where the authors search for conductivity through films of PDMS of thicknesses 1 to 3 μm with various types of electrodes. They observed conduction with resistances of the order of 1 to a few Ω for some electrode configurations but not for others. It appears that whether conduction is seen depends on whether or not the electrode configuration is such that the electrodes exert some pressure on the films. This is consistent with the view of Grigorov and coworkers (see e.g. [23, 24]) that pressure tends to align conducting channels through the film.

Personally I think that, of the three systems I have discussed, if one is prepared for some time-dependent properties, the materials problems seem to be easiest for the polymers. Some suggestions for possible new experiments on OAPP films are made in subsection 14.15 of [21].

Acknowledgement

I should like to thank A.S. Alexandrov for correspondence regarding H_{c1} in bosonic superconductors.

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